

Multicomponent, Multiphase Thermodynamics of Swelling Porous Media with Electroquasistatics: I. Macroscale Field Equations

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Abstract

A systematic development of the macroscopic field equations (conservation of mass, linear and angular momentum, energy, and Maxwell's equations) for a multiphase, multicomponent medium is presented. It is assumed that speeds involved are much slower than the speed of light and that the magnitude of the electric field significantly dominates over the magnetic field so that the electroquasistatic form of Maxwell's equations applies. A mixture formulation is presented for each phase and then averaged to obtain the macroscopic formulation. Species electric fields are considered, however it is assumed that it is the total electric field which contributes to the electrically induced forces and energy. The relationships between species and bulk phase variables and the macroscopic and microscopic variables are given explicitly. The resulting field equations are of relevance to many practical applications including, but not limited to, swelling clays (smectites), biopolymers, biological membranes, pulsed electrophoresis, and chromatography.

Key words: porous media, mixture theory, electrodynamics, averaging, swelling

1 Introduction

We attempt to address the following issue: in a composite or porous medium, how do the electro-thermodynamic variables of each individual constituent contribute to the electro-thermodynamic variables of the mixture as a whole? In other words, given information about individual materials, determine the relationship between the electro-thermodynamic properties of individual components and the electro-thermodynamic properties of the averaged multi-phase

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multi-component material. We combine mixture theory and averaging to obtain macroscopic field equations for a deformable porous medium in which species may induce different electric fields but forces on the species are determined by the net electric field of the mixture.

The constituent forms of Maxwell's equations were first developed by Kelly [24], although he did not consider deformable media. A binary mixture of electro-magnetic fluids has been used to model plasma with single electric and magnetic fields, see e.g. Kulsrud [25]. Benach and Müller [2] applied single electric and magnetic fields to model a mixture of dielectric fluids. The idea of using multiple electric fields has been used historically in modeling a binary mixture of superconducting fluids [9]. Eringen [14] developed a mixture theoretic approach for a multiple constituent electro-magnetic deformable medium with multiple electro-magnetic fields and applied the model to combinations of conducting/superconducting fluids and elastic solids. This article differs from [14] in that multiple phases are considered, a different philosophy is taken in the electric fields of constituents accounting for energy and momentum balance, and the mixture may swell. Mixture theory alone does not allow for this development. An upscaling approach is required to map microscopic information into well-defined macroscopic variables.

On the microscale one can distinguish between phases or materials, while the macroscale is defined to be the scale at which the material appears to be homogeneous. There are several upscaling techniques to choose between: homogenization (matched asymptotics) [5, 12, 35], volume averaging in the sense of Whitaker [31, 33, 34, 41, 42], spectral integral methods [17], generalized Taylor-Aris methods [7], and hybrid mixture theory [1, 3, 21, 22]. All but the latter of these methods upscale field equations and constitutive equations from the microscale to the macroscale. The hybrid mixture theoretic approach that we adapt does not upscale constitutive relations.

We present constituent, or species, electro-quasistatic equations for a mixture, give the relationship between the species and single-phase properties, and then volume average these governing equations for a multicomponent, multiphase medium to obtain the governing equations for the medium at the macroscale. At this scale, the medium is viewed as a continuum where thermodynamic properties for each constituent of each phase exist spatially everywhere. The relationships between the microscale variables and the macroscale variables are explicitly given. For ease of exposition we assume that interfacial properties such as excess mass density, free charge on interfaces, and interface currents, are negligible; although the present theory can be extended to incorporate these effects [19]. The medium is referred to as multi-phase, but it is understood that this includes composites (e.g. a medium composed of two solid materials), or a porous medium, where the multiphases may be gas, immiscible liquids, and/or solid.

Maxwell's equations involve species electric fields, but the macroscale momentum and energy equations for species are based on the philosophy that the force or work induced by the electric field acting on a species is generated by the *total* electric field. This differs from what has been done in the past [14, 24].

The species electric fields are defined through Gauss' Law since the charge and polarization density are well defined for a species. The species electric fields then manifest themselves in the macroscale equations through terms involving gradients or time-rate-of-change of the volume fraction.

The resulting field equations may be used to obtain restrictions on admissible constitutive relations by applying the methods of either extended thermodynamics [30], or rational thermodynamics [13, 10]. The need for these equations, and the explicit relationships between the macroscopic and microscopic variables is demonstrated by the increasingly complex porous media being studied. Recent examples include Huyghe and Janssen [23] and Gu *et al.* [20] who both use a simplified version of the equations developed herein to model an incompressible porous medium composed of an electrically charged solid phase saturated with an ionic fluid.

2 Microscale Equations

In this section we present the governing field equations at the microscale. The equations include mass balance, conservation of linear and angular momentum, conservation of energy, entropy balance, and Maxwell's equations. The complete form of these equations for a bulk phase (single phase with no species) are given by Eringen [15] and Tiersten [38], and here we follow their formulation and notation. The derivation of these equations follows from the particle level in the spirit of Lorentz [27].

It is assumed that the dominant field source is the electric field and that velocities are small compared to the speed of light (non-relativistic). Following Melcher [28], the electroquasistatic system of equations are obtained by non-dimensionalizing Maxwell's equations, expanding each variable in a Taylor series about the variable representing the ratio of the electromagnetic wave transit time to the characteristic time of the problem, and taking the zero-order equations as the quasi-static formulation. The difference between the electroquasistatic formulation and the magneto-quasistatic formulation arises in the choice of the normalizing parameters: in the former a reference electric field is used, and in the latter a reference magnetic field is used.

It is necessary to postulate governing field equations which hold for each specie. Following Truesdell [40], we adhere to the following principles: (1) all properties of the mixture must be mathematical consequences of properties of the constituents; (2) to describe the motion of a constituent, we may perceive it as being isolated from the rest of the mixture, provided we allow properly for the actions of the other constituents; (3) the motion of the mixture is governed by the same equations as is a single body. Further, due to the incorporation of electric fields, some assumptions must be made regarding the form of the momentum and energy balance laws. It is assumed that (4) the "primitive" form of the balance laws is the one incorporating the work and force, and not, e.g. the electro-stress tensors. This is in contrast to [8, 26] in which the electro-magnetic stresses are considered the primitive quantity. The forms are equivalent up to the

classical Maxwell's equations, but are not equivalent in the mixture formulation. Hence, until experiments prove otherwise, the choice is purely philosophical. The last principle is that (5) within the electrical work and force terms in the energy and momentum balance equations respectively, it is the *total* electric field which acts on the species, and not just the electric field associated with the species. This last assumption guarantees that principles (1), (2), and (3) are not violated.

Although the form of the equations for the constituents is natural for some balance laws (conservation of mass, conservation of charge density), it leads to un-intuitive variables in other equations, e.g. the partial stress tensor. However, we do not want to mix bulk phase equations with constitutive equations, and hence formulate constitutive equations for all field equations. To account for the effects of the other constituents, exchange terms, denoted by variables with a carrot $\hat{\cdot}$, are introduced.

The species' equations can then be summed to obtain the governing equation for the phase, and the relationship between the species properties and their bulk phase counterparts are then obtained. The details regarding this procedure for the field equations with no electric or magnetic effects can be found in Truesdell and Toupin [39] or Bowen [6]. For the parallel development of Maxwell's equations, see Kelly [24].

We now present the governing equations for a mixture in a single phase at the microscale assuming electroquasistatics. The relationships between the species' variables and the bulk phase variables are obtained by summing the field equation over all constituents and relating the variables so as to obtain the field equation at the bulk scale. These relationships are given in Appendix B.

Conservation of Mass

$$\frac{D^j(\rho^j)}{Dt} + \rho^j(\nabla \cdot \mathbf{v}^j) = \rho^j \hat{r}^j \quad (1)$$

where $\frac{D^j}{Dt}$ is the material time derivative given by

$$\frac{D^j}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^j \cdot \nabla \quad (2)$$

and where \hat{r}^j is the rate of mass transfer to species j from other species due to chemical reactions. Summing over constituents we obtain the bulk phase equation

$$\frac{D\rho}{Dt} + \rho(\nabla \cdot \mathbf{v}) = 0 \quad (3)$$

with the restriction

$$\sum_{j=1}^N \rho^j \hat{r}^j = 0. \quad (4)$$

This restriction merely states that within an isolated system consisting of a single phase there is no net loss of mass.

Gauss' Law

For this equation we introduce the electric field for species j , \mathbf{E}^j . Gauss' law for constituent j can then be expressed as

$$\nabla \cdot \mathbf{D}^j - q_e^j = \hat{d}^j \quad (5)$$

where \mathbf{D}^j is the displacement vector for the j th component only, q_e^j is the charge density of constituent j , and \hat{d}^j is the excess charge density due to the presence of other species. The displacement vector for constituent j is defined in terms of the electric field and polarization density as:

$$\mathbf{D}^j = \varepsilon_0 \mathbf{E}^j + \mathbf{P}^j, \quad (6)$$

where ε_0 is the permittivity in a vacuum. In MKS units, the permittivity has the value of 8.854×10^{-12} Farads per meter [28].

The species' electric field, \mathbf{E}^j , must satisfy the restriction that the total electric field, \mathbf{E} , is the sum of the species' electric field, i.e. $\sum_{j=1}^N \mathbf{E}^j = \mathbf{E}$. If there is no external electric field then \mathbf{E} is just the electric field generated by all the species. There is no unique way of incorporating the externally applied electric field into these equations. One could treat the external electric field as the presence of another species, say species N , in which this "external" species has no other electro-thermodynamic properties. Then species N would have no charge density, no associated polarization, etc. and these terms would be set to zero in the governing equations. Alternately, a portion of the external field could be assigned to each \mathbf{E}^j so that \mathbf{E}^j is the sum of the electric field generated by species j and a weight, w^j , times the external electric field. The weights must sum to one, and may, for example, be proportional to the amount of charge, or maybe the mass fraction of species j . A third choice might be to define the species electric field so that the exchange term \hat{d}^j is zero. This simplifies computations down the road although its physical interpretation is not clear. These choices have no affect on the following derivation, as long as \mathbf{E}^j sum to the total electric field. However, in formulating a mathematical model it is necessary to choose a particular definition and remain consistent.

Summing over constituents gives the bulk phase Gauss law:

$$\nabla \cdot \mathbf{D} - q_e = 0 \quad (7)$$

where $\mathbf{D} = \sum_{j=1}^N \mathbf{D}^j$ and with the restriction

$$\sum_{j=1}^N \hat{d}^j = 0. \quad (8)$$

which states that the net effect of excess charge densities produced by the species acting on each other must sum to zero.

Faraday's Law

Faraday's law for the quasi-static case for species j is given by

$$\nabla \times \mathbf{E}^j = \hat{\boldsymbol{\sigma}}^j \quad \text{or} \quad E_{k,l}^j - E_{l,k}^j = \varepsilon_{lkm} \hat{\sigma}_m^j, \quad (9)$$

where the second form of the equation is in indicial notation with repeated indices denoting summation, a comma denotes differentiation, and ε_{lkm} is the permutation tensor. Here $\hat{\boldsymbol{\sigma}}^j$ incorporates the effect of the electric fields, \mathbf{E}^i , $i \neq j$.

Summing over species gives the bulk phase Faraday's law,

$$\nabla \times \mathbf{E} = \mathbf{0}, \quad (10)$$

where $\mathbf{E} = \sum_{j=1}^N \mathbf{E}^j$ is the total electric field. This relationship is assumed throughout. The required restriction obtained from this summation is that

$$\sum_{j=1}^N \hat{\boldsymbol{\sigma}}^j = \mathbf{0}. \quad (11)$$

Ampère's Law

Ampère's law for the quasi-static case for species j is given by

$$\mathbf{J}^j = -\frac{\partial \mathbf{D}^j}{\partial t} + \nabla \times \mathbf{H}^j - \nabla \times (\mathbf{P}^j \times \mathbf{v}^j) + \hat{\mathbf{h}}^j \quad (12)$$

where \mathbf{H}^j is the magnetic field intensity and $\hat{\mathbf{h}}^j$ accounts for the effects of other constituents.

Summing over species gives the bulk phase version of this law,

$$\mathbf{J} = -\frac{\partial \mathbf{D}}{\partial t} + \nabla \times c\mathbf{H} - \nabla \times (\mathbf{P} \times \mathbf{v}) \quad (13)$$

where

$$\sum_{j=1}^N \hat{\mathbf{h}}^j = \mathbf{0}. \quad (14)$$

Conservation of Electric Charge

This equation can be derived by taking the divergence of Ampère's law and the time derivative of Gauss' Law and summing the results. Of all Maxwell's equations, this equation is the most accepted in mixture form since each component has a well defined physical interpretation. The conservation of electric charge for species j is

$$\nabla \cdot (\mathcal{J}^j + q_e^j \mathbf{v}^j) + \frac{\partial q_e^j}{\partial t} = \hat{q}^j + \rho^j z^j \hat{r}^j, \quad (15)$$

where \mathbf{v}^j is the velocity of species j relative to a fixed frame of reference, \mathcal{J}^j is the free current density of constituent j measured relative to species j , z^j is the charge per unit mass and \hat{q}^j is the rate of gain of charge density due to the presence of other constituents but not due to chemical reactions. The free current density, denoted by \mathcal{J}^j , is related to the free current density relative to a fixed (Eulerian) frame of reference, \mathbf{J}^j , by

$$\mathcal{J}^j = \mathbf{J}^j - q_e^j \mathbf{v}^j. \quad (16)$$

Another form of this equation is obtained by subtracting out the conservation of mass to reduce redundancy, and this yields

$$\rho^j \frac{D^j z^j}{Dt} + \nabla \cdot \mathcal{J}^j = \hat{q}^j. \quad (17)$$

Summing over constituents yields

$$\nabla \cdot (\mathcal{J} + q_e \mathbf{v}) + \frac{\partial q_e}{\partial t} = 0, \quad (18)$$

where

$$\sum_{j=1}^N [\hat{q}^j + \rho^j z^j \hat{r}^j] = 0. \quad (19)$$

This equation states that the net gain or loss of total charge of constituent j due to ion transfer or chemical reactions is zero in an isolated system.

In addition, because of the coupling between Gauss' law, Ampère's law, and the conservation of charge, there is a coupling between the exchange terms:

$$\nabla \cdot \hat{\mathbf{h}}^j - \frac{\partial \hat{d}^j}{\partial t} = \hat{q}^j + q_e^j \hat{r}^j.$$

Linear Momentum Balance

This equation is given by

$$\rho^j \frac{D^j \mathbf{v}^j}{Dt} - \nabla \cdot \mathbf{t}^j - \rho^j \mathbf{g}^j - q_e^j \mathbf{E} - \mathbf{P}^j \cdot \nabla \mathbf{E} = \rho^j \hat{\mathbf{i}}^j \quad (20)$$

where \mathbf{t}^j is the partial Cauchy stress tensor and \mathbf{g}^j is the external body force acting on constituent j . The exchange term, $\hat{\mathbf{i}}^j$, takes into account all gain of momenta due to the presence of other species but not due to chemical reactions. The last term on the left-hand-side is usually referred to as the Kelvin force, and the adjacent term (on the LHS) is referred to as the Lorentz force [15]. Note that unlike [14, 24] we assume it is the *total* electric field which contributes to these forces.

Summing over constituents gives the conservation of linear momentum for the entire phase,

$$\rho \frac{D\mathbf{v}}{Dt} - \nabla \cdot \mathbf{t} - \rho \mathbf{g} - q_e \mathbf{E} - \mathbf{P} \cdot \nabla \mathbf{E} = \mathbf{0}. \quad (21)$$

In this form \mathbf{t} is the Cauchy stress tensor and is related to the partial Cauchy stress tensors, \mathbf{t}^j , in the same way as the purely thermo-mechanical mixture theory (no electric field). This is what naturally appears in the energy conservation equation given below, i.e. if other terms are incorporated into the definition of the bulk phase stress tensor, then these additional terms must be subtracted out where the stress tensor appears in the conservation of energy and the restriction must be modified. The specific relationship between the constitutive variables and the bulk phase variables are given in Appendix B. The restriction for the conservation of linear momentum is:

$$\sum_{j=1}^N [\rho^j \hat{\mathbf{t}}^j + \rho^j \mathbf{v}^j \hat{\mathbf{r}}^j] = \mathbf{0} \quad (22)$$

The restriction states that the net momentum gained between species due to mass transfer or mechanical momentum must be zero.

Angular Momentum Balance

In indicial notation, the angular momentum equation is

$$\epsilon_{klm} t_{kl}^j + \epsilon_{klm} P_k^j E_l = -\rho^j \hat{m}_m^j, \quad (23)$$

where \hat{m}_m^j is the m th component of the net rate of gain of angular momentum due to the presence of other species. The negative sign on the right hand side is in keeping with the convention that exchange terms (in this case $\hat{\mathbf{m}}^j$) represents a rate of *gain* of a property.

Summing over constituents yields

$$\epsilon_{klm} t_{kl} + \epsilon_{klm} P_k E_l = 0_m \quad (24)$$

with the restriction that

$$\sum_{j=1}^N \rho^j \hat{\mathbf{m}}^j = \mathbf{0}. \quad (25)$$

This equation states that the net internal angular momentum for this single-phase medium, consisting of the sum of angular momenta generated by species acting on each other, must be zero.

Conservation of Energy

The species energy balance is

$$\begin{aligned} \rho^j \frac{D^j e^j}{Dt} - \mathbf{t}^j : \nabla \mathbf{v}^j - \nabla \cdot \mathbf{q}^j - \rho^j h^j - \mathcal{J}^j \cdot \mathbf{E} - \frac{\partial \mathbf{P}^j}{\partial t} \cdot \mathbf{E} \\ - [\nabla \cdot (\mathbf{v}^j \mathbf{P}^j)] \cdot \mathbf{E} = \rho^j \hat{Q}^j \end{aligned} \quad (26)$$

where the colon indicates a tensor dot product (e.g. $\underline{\mathbf{a}}:\underline{\mathbf{b}} = \sum_{i,j} a_{ij} b_{ij}$) and \hat{Q}^j is the rate of energy gain due to the presence of other constituents but not due to chemical reactions (mass transfer) or momentum transfer. The sum of the last

three terms on the left-hand-side is the electrical energy source. As in the linear momentum balance we assume that electric energy is due to the *total* electric field, not just part of it. These three terms take on a variety of forms [15, 28] which are related through the Maxwell equations (Gauss' law, Faraday's law, Ampère's Law, and Conservation of Electric Charge). The form presented here is the one derived directly from microscale electrical forces using a statistical averaging approach (see Eringen [15]) making no use of Maxwell's equations, since otherwise exchange terms (\hat{d}^j , $\hat{\sigma}^j$, \hat{q}^j) appear.

Summing over constituents yields

$$\rho \frac{De}{Dt} - \mathbf{t} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} - \rho h - \mathcal{J} \cdot \mathbf{E} - \frac{\partial \mathbf{P}}{\partial t} \cdot \mathbf{E} - [\nabla \cdot (\mathbf{v} \mathbf{P})] \cdot \mathbf{E} = 0 \quad (27)$$

with the restriction

$$\sum_{j=1}^N \left[\rho^j \hat{Q}^j + \rho^j \mathbf{v}^j \cdot \hat{\mathbf{i}}^j + (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \rho^j \hat{r}^j \right] = 0. \quad (28)$$

Entropy Balance

The entropy balance equation is one way of representing the second law of thermodynamics:

$$\rho^j \frac{D^j \eta^j}{Dt} - \nabla \cdot \phi^j - \rho^j b^j = \rho^j \hat{\eta}^j + \rho^j \hat{\Lambda}^j \quad (29)$$

where $\hat{\eta}^j$ is the rate of transfer of entropy from other constituents. Here $\hat{\Lambda}^j$ is the rate at which entropy is generated.

Summing over constituents yields

$$\rho \frac{D\eta}{Dt} - \nabla \cdot \phi - \rho b = \rho^j \hat{\Lambda} \quad (30)$$

with the restriction

$$\sum_{j=1}^N \left[\rho^j \hat{\eta}^j + \rho^j \mathbf{v}^j \hat{r}^j \right] = 0. \quad (31)$$

It is postulated that the total rate of entropy generation, obtained by summing over all species, is non-negative. All relations for this equation remain unaltered from the purely thermo-mechanical mixture theory.

3 Macroscale Equations

In this section we average the microscale equations and obtain equations at the macroscale. At the macroscale, each thermodynamic variable is defined spatially everywhere, so that if there are 3 phases, with each phase containing N constituents, the medium is viewed as $3N$ overlaying continua. The first subsection discusses the notation and assumptions required to upscale, and the following

subsections present the macroscale field equations and how each variable relates to the microscale. To the authors' knowledge, the electroquasistatic equations have not been presented before.

3.1 Averaging Procedure

Consider a multi-constituent multi-phase medium where the phase is denoted by Greek letters (α, β, γ), and the constituent or species is denoted by j , $j = 1, \dots, N$. For ease of exposition we assume that interfaces contain no thermodynamic properties. Consequently it is assumed no amount of mass, momentum, energy, charge, current, etc. is lost when being transferred between phases. Interfacial effects can be included by pursuing any of the approaches of [18, 19, 29], however, we shall omit these terms to keep the level of algebra at a minimum.

The governing microscopic equations for each phase were given in Section 2, but to distinguish between phases we introduce the additional Greek superscript.

Assuming no surface discontinuities, the constituent, microscopic field equations of mass, charge, linear momentum, angular momentum, energy, and entropy can be expressed for a given phase, α , as (following the notation of Eringen, [13]):

$$\frac{\partial}{\partial t}(\rho^j \psi^j) + \nabla \cdot (\rho^j \mathbf{v}^j \psi^j) - \nabla \cdot \mathbf{i}^j - \rho^j f^j - F^j = \rho^j G^j + \rho^j \hat{\psi}^j \quad (32)$$

where ψ^j is the mass-average (over the phase) thermodynamic property of constituent j , \mathbf{v}^j is the mass-average velocity vector, ρ^j is the mass density, \mathbf{i}^j is the flux vector, f^j is the body source, F^j is the supply due to electrical effects, G^j is the net production, and $\hat{\psi}^j$ represents the influx of ψ from all other constituents (e.g. due to chemical reactions). If there is only one constituent, $\hat{\psi}^j$ is zero. For each of the respective equations, the quantities given in Table 1 are used.

Table 1: Quantities for Equation (32)

Quantity	ψ	\mathbf{i}	f	F	$\hat{\psi}$	G
Mass	1	$\mathbf{0}$	0	0	\hat{r}	0
Charge	z	\mathcal{J}	0	0	$\hat{q} + \rho z \hat{r}$	0
Linear Momentum	\mathbf{v}	\mathbf{t}	$\mathbf{g} + \mathbf{g}_I$	\mathbf{F}_e	$\hat{\mathbf{i}} + \hat{r} \mathbf{v}$	0
Angular Momentum	$\mathbf{r} \times \mathbf{v}$	$\mathbf{r} \times \mathbf{t}$	$\mathbf{r} \times \mathbf{g}$	$\mathbf{r} \times \mathbf{F}_e + \mathbf{C}_e$	$\mathbf{r} \times (\hat{\mathbf{i}} + \hat{r} \mathbf{v})$	0
Energy	$e + \frac{1}{2} v^2$	$\mathbf{t} \mathbf{v} + \mathbf{q}$	$\mathbf{g} \cdot \mathbf{v} + h$	W_e	$\hat{Q} + \hat{\mathbf{i}} \cdot \mathbf{v} + \hat{r}(e + \frac{1}{2} v^2)$	0
Entropy	η	ϕ	b	0	$\hat{\eta} + \hat{r} \mathbf{v}$	Λ

For conciseness we also introduce the force, couple, and work due to the electric field, respectively:

$$\mathbf{F}_e^j = q_e^j \mathbf{E} + \mathbf{P}^j \cdot \nabla \mathbf{E} \quad (33)$$

$$= -\nabla \cdot \left(\mathbf{D}^j \mathbf{E} - \frac{1}{2} \varepsilon_o \mathbf{E}^j \cdot \mathbf{E} \mathbf{I} \right) + \tilde{\mathbf{d}}^j \mathbf{E} + \frac{1}{2} \varepsilon_o (\nabla \mathbf{E} \cdot \mathbf{E}^j - \nabla \mathbf{E}^j \cdot \mathbf{E}) \quad (34)$$

$$\mathbf{C}_e^j = \mathbf{P}^j \times \mathbf{E} \quad (35)$$

$$W_e^j = \mathbf{J}^j \cdot \mathbf{E} + \frac{\partial \mathbf{P}^j}{\partial t} \cdot \mathbf{E} + \nabla \cdot (\mathbf{v}^j \mathbf{E} \cdot \mathbf{P}^j) \quad (36)$$

$$\begin{aligned} &= \frac{\partial}{\partial t} \left(-\frac{1}{2} \varepsilon_o \mathbf{E}^j \cdot \mathbf{E} \right) - \nabla \cdot (\mathbf{E} \times \mathbf{H}^j) + \nabla \cdot (\mathbf{P}^j \mathbf{v}^j \cdot \mathbf{E}) \\ &\quad + \tilde{\mathbf{h}}^j \cdot \mathbf{E} - \frac{1}{2} \varepsilon_o \left(\frac{\partial \mathbf{E}^j}{\partial t} \cdot \mathbf{E} - \frac{\partial \mathbf{E}}{\partial t} \cdot \mathbf{E}^j \right) \end{aligned} \quad (37)$$

(see also equations (20,23,26)). Definitions of all terms are given in Appendix A. The forms of \mathbf{F}_e^j and W_e^j are a consequence of which form one assumes to be the most primitive. If one assumes that the second forms of \mathbf{F}_e^j and W_e^j , (34, 37), are the most primitive then miscellaneous terms would appear in the first forms. The two forms are needed in order to obtain conditions which correspond directly with jump boundary conditions across an interface. The averaging procedure is based on ideas laid down in [16, 41, 42, 37]. Several methods are available, but we choose the computationally simplest. Equations are averaged by weighted integration using the indicator function of the α -phase. To avoid the mathematical difficulties of, for example, defining a derivative of the averaged quantities resulting from using such a weighting function, one must treat the averaged quantity as a distribution [36, 32].

It should be noted that using this simple weight function may mean that the averaged value may not represent the actual values being measured. To account for the measuring technique, one needs to choose a weight function which represents the instrument used to measure the physical properties [11]. Extensions of the presented theory to such cases are straight forward.

Let δV be a volume, δV_α the portion of δV in the α -phase, and $\delta A_{\alpha\beta}$ the portion of the interface within δV . It is assumed that δV_α and $\delta A_{\alpha\beta}$ are isolated simply connected regions. If the magnitude of δV is denoted by $|\delta V|$ then the volume fraction can be expressed as

$$\varepsilon^\alpha(\mathbf{x}, t) = \frac{|\delta V_\alpha|}{|\delta V|} \quad (38)$$

so that

$$\sum_\alpha \varepsilon^\alpha = 1. \quad (39)$$

The indicator function is

$$\gamma_\alpha(\mathbf{r}, t) = \begin{cases} 1 & \text{if } \mathbf{r} \in \delta V_\alpha \\ 0 & \text{if } \mathbf{r} \in \delta V_\beta, \quad \beta \neq \alpha. \end{cases}$$

We may write $\mathbf{r} = \mathbf{x} + \boldsymbol{\xi}$ where \mathbf{x} is the macroscale spatial variable, and $\boldsymbol{\xi}$ varies over δV . To obtain the macroscale equations formally, one multiplies

equation (2) by $\gamma_\alpha(\mathbf{r})$, integrates over δV with respect to $\boldsymbol{\xi}$ (\mathbf{x} is held fixed) and divides by $|\delta V|$. Then in order to obtain equations of the forms which mirror the microscale equations, the following theorem is applied to interchange the order of differentiation and integration.

Theorem 1 *If $\mathbf{w}_{\alpha\beta}$ is the microscopic velocity of interface $\alpha\beta$ and \mathbf{n}_α is the outward unit normal vector of δV_α indicating the integrand should be evaluated in the limit as the $\alpha\beta$ -interface is approached from the α -side then*

$$\begin{aligned} \frac{1}{|\delta V|} \int_{\delta V} \frac{\partial f}{\partial t} \gamma_\alpha dv(\boldsymbol{\xi}) &= \frac{\partial}{\partial t} \left[\frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv(\boldsymbol{\xi}) \right] \\ &\quad - \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} f \mathbf{w}_{\alpha\beta} \cdot \mathbf{n}_\alpha da(\boldsymbol{\xi}) \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{1}{|\delta V|} \int_{\delta V} \nabla \mathbf{r} f \gamma_\alpha dv(\boldsymbol{\xi}) &= \nabla \mathbf{x} \left[\frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv(\boldsymbol{\xi}) \right] \\ &\quad + \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} f \mathbf{n}_\alpha da(\boldsymbol{\xi}). \end{aligned} \quad (41)$$

After averaging equation (32), the system is considered to be a mixture so that each component in each phase and each bulk phase now have thermodynamic properties existing at each point within the macroscopic body. The macroscopic definition of each field variable in terms of its microscopic counterpart, making *no small perturbation assumptions*, is given in Appendix C.

For more details regarding this procedure for the field equations with no electric or magnetic effects see for example Whitaker [41], Slattery [37] and Plumb and Whitaker [31]. For the parallel development of Maxwell's equations with constitutive assumptions, see Rio and Whitaker [33, 34].

3.2 Macroscopic Conservation Equations

Conservation of Mass

The macroscopic mass balance for constituent j in phase α is

$$\frac{D^{\alpha_j}(\varepsilon^\alpha \rho^{\alpha_j})}{Dt} + \varepsilon^\alpha \rho^{\alpha_j} (\nabla \cdot \mathbf{v}^{\alpha_j}) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \widehat{e}_\beta^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} \widehat{r}^{\alpha_j} \quad (42)$$

where $\frac{D^{\alpha_j}}{Dt}$ is the material time derivative given by

$$\frac{D^{\alpha_j}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\alpha_j} \cdot \nabla, \quad (43)$$

and $\widehat{e}_\beta^{\alpha_j}$ represents the net rate of mass gained by constituent j in phase α from phase β :

$$\widehat{e}_\beta^{\alpha_j} = \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da, \quad (44)$$

where $\mathbf{w}_{\alpha\beta}^j$ is the velocity of species j at interface $\alpha\beta$.

The bulk phase counterpart is given by

$$\frac{D^\alpha(\varepsilon^\alpha \rho^\alpha)}{Dt} + \varepsilon^\alpha \rho^\alpha (\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \hat{e}_\beta^\alpha. \quad (45)$$

The net gain of mass of the bulk phase must be zero, implying that:

$$\sum_{j=1}^N \rho^{\alpha j} \hat{r}^{\alpha j} = 0 \quad \forall \alpha. \quad (46)$$

Further, since the interface is assumed to be massless, we have the restriction:

$$\varepsilon^\alpha \rho^{\alpha j} \hat{e}_\beta^{\alpha j} + \varepsilon^\beta \rho^{\beta j} \hat{e}_\alpha^{\beta j} = 0, \quad j = 1, \dots, N. \quad (47)$$

Using (45) we can re-write (42) as

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha C^{\alpha j}}{Dt} + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha}) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} (\hat{e}_\beta^{\alpha j} - \hat{e}_\beta^\alpha) + \varepsilon^\alpha \rho^{\alpha j} \hat{r}^{\alpha j}. \quad (48)$$

Gauss' Law

The macroscopic form of Gauss' law for constituent j in phase α is

$$\nabla \cdot (\varepsilon^\alpha \mathbf{D}^{\alpha j}) - \varepsilon^\alpha q_e^{\alpha j} = \varepsilon^\alpha \hat{d}^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{d}_\beta^{\alpha j} \quad (49)$$

where $\mathbf{D}^{\alpha j}$ is the volume average of \mathbf{D}^j . Here $\hat{d}_\beta^{\alpha j}$ represents the effect constituent j in phase β has on the charge of the same constituent in phase α :

$$\hat{d}_\beta^{\alpha j} = -\frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \mathbf{D}^j \cdot \mathbf{n}^\alpha da. \quad (50)$$

Other relations are given in Appendix C.

Summing over j yields the bulk phase form:

$$\nabla \cdot (\varepsilon^\alpha \mathbf{D}^\alpha) - \varepsilon^\alpha q_e^\alpha = \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{d}_\beta^\alpha. \quad (51)$$

The restrictions include

$$\sum_{j=1}^N \hat{d}^{\alpha j} = 0 \quad \forall \alpha \quad (52)$$

$$\varepsilon^\alpha \hat{d}_\beta^{\alpha j} + \varepsilon^\beta \hat{d}_\alpha^{\beta j} = 0, \quad j = 1, \dots, N. \quad (53)$$

The first restriction states that the net effect constituents have on each other within phase α must be zero, and the second states that the interfacial displacement is zero, which is a consequence of assuming that the interface contains no

electric/thermodynamical properties. Recall that if there is no surface charge or polarization the jump condition between two materials states that the jump in the normal component of the displacement vector must be zero [15]:

$$\mathbf{n} \cdot [[\mathbf{D}]] = 0. \quad (54)$$

Integrating this equation over $\delta A_{\alpha\beta}$ shows that this theory is consistent with the classical formulation for the jump condition, equation (53).

Faraday's Law

The macroscopic form of Faraday's law for constituent j in phase α is

$$\nabla \times (\varepsilon^\alpha \mathbf{E}^{\alpha j}) = \varepsilon^\alpha \hat{\boldsymbol{\sigma}}^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{\boldsymbol{\sigma}}_\beta^{\alpha j} \quad (55)$$

or in indicial notation

$$(\varepsilon^\alpha E_k^{\alpha j})_{,l} - (\varepsilon^\alpha E_l^{\alpha j})_{,k} = \varepsilon_{lkm} \varepsilon^\alpha \hat{\sigma}_m^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon_{lkm} \varepsilon^\alpha (\hat{\sigma}_\beta^{\alpha j})_m \quad (56)$$

where

$$\hat{\sigma}_\beta^{\alpha j} = -\frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \mathbf{n}^\alpha \times \mathbf{E}^j da, \quad (57)$$

which represents the effect phase β has on the electric field of phase α . Upon summing, the bulk phase form of Faraday's law becomes:

$$\nabla \times (\varepsilon^\alpha \mathbf{E}^\alpha) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{\boldsymbol{\sigma}}_\beta^\alpha \quad (58)$$

with restrictions

$$\sum_{j=1}^N \hat{\boldsymbol{\sigma}}^{\alpha j} = 0 \quad \forall \alpha \quad (59)$$

$$\varepsilon^\alpha \hat{\boldsymbol{\sigma}}_\beta^{\alpha j} + \varepsilon^\beta \hat{\boldsymbol{\sigma}}_\alpha^{\beta j} = 0 \quad j = 1, \dots, N. \quad (60)$$

Equation (60) corresponds precisely with the classical jump condition across interfaces [15]

$$\mathbf{n} \times [[\mathbf{E}]] = \mathbf{0}, \quad (61)$$

where the double square brackets indicate the difference of the quantity evaluated on either side of the interval, if (61) is integrated over the surface $\delta A_{\alpha\beta}$.

Ampère's Law The macroscopic form of Ampère's law for the quasi-static case for species j of phase α is given by

$$\varepsilon^\alpha \mathbf{J}^{\alpha_j} = -\frac{\partial(\varepsilon^\alpha \mathbf{D}^{\alpha_j})}{\partial t} + \nabla \times (\varepsilon^\alpha \mathbf{H}^{\alpha_j}) - \nabla \times (\varepsilon^\alpha \mathbf{P}^{\alpha_j} \times \mathbf{v}^{\alpha_j}) + \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{\mathbf{h}}_\beta^{\alpha_j} + \varepsilon^\alpha \hat{\mathbf{h}}^{\alpha_j} \quad (62)$$

where

$$\hat{\mathbf{h}}_\beta^{\alpha_j} = \frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{D}^j \mathbf{w}_{\alpha\beta}^j \cdot \mathbf{n}^\alpha - (\mathbf{H}^j - \mathbf{P}^j \times \mathbf{v}^j) \times \mathbf{n}^\alpha \right] da \quad (63)$$

represents the effect of phase β on phase α . Summing over species gives the bulk phase version of this law,

$$\varepsilon^\alpha \mathbf{J}^\alpha = -\frac{\partial(\varepsilon^\alpha \mathbf{D}^\alpha)}{\partial t} + \nabla \times \varepsilon^\alpha \mathbf{H}^\alpha - \nabla \times (\varepsilon^\alpha \mathbf{P}^\alpha \times \mathbf{v}^\alpha) + \sum_{\beta \neq \alpha} \varepsilon^\alpha \hat{\mathbf{h}}_\beta^\alpha \quad (64)$$

where the restrictions are

$$\sum_{j=1}^N \hat{\mathbf{h}}^{\alpha_j} = \mathbf{0} \quad \forall \alpha \quad (65)$$

$$\varepsilon^\alpha \hat{\mathbf{h}}_\beta^{\alpha_j} + \varepsilon^\beta \hat{\mathbf{h}}_\alpha^{\beta_j} = \mathbf{0} \quad j = 1, \dots, N. \quad (66)$$

The jump condition associated with Ampère's law is given by [15]:

$$\mathbf{n} \times [[\mathbf{H} - \mathbf{w} \times \mathbf{D}]] = \mathbf{0} \quad (67)$$

where the polarization at the surface has been neglected. Equation (63) does not correspond directly with the jump condition given in [15] since (67) is derived directly from the global surface area form of Ampère's law, and (63) is derived from the bulk-phase form of the law. This causes a loss of information; specifically, (63) does not include a term corresponding to $\mathbf{w}^j(\mathbf{n} \cdot \mathbf{D}^j)$.

Conservation of Electric Charge

The conservation of charge equation at the macroscale becomes

$$\begin{aligned} \nabla \cdot (\varepsilon^\alpha \mathcal{J}^{\alpha_j} + \varepsilon^\alpha q_e^{\alpha_j} \mathbf{v}^{\alpha_j}) + \frac{\partial}{\partial t} (\varepsilon^\alpha q_e^{\alpha_j}) &= \varepsilon^\alpha \hat{q}^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} z^{\alpha_j} \hat{r}^{\alpha_j} \\ &+ \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} (\hat{Z}_\beta^{\alpha_j} + z^{\alpha_j} \hat{e}_\beta^{\alpha_j}) \end{aligned} \quad (68)$$

where

$$\begin{aligned} \hat{Z}_\beta^{\alpha_j} &= \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[q_e^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) - \mathcal{J}^j \right] \cdot \mathbf{n}^\alpha da \\ &- \frac{z^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \end{aligned} \quad (69)$$

which represents the rate of exchange of charge of constituent j from phase β to phase α not due to mass exchange. Using the continuity equation, (42), equation (68) may be re-written as:

$$\varepsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j} z^{\alpha_j}}{Dt} + \nabla \cdot (\varepsilon^\alpha \mathcal{J}^{\alpha_j}) = \varepsilon^\alpha \hat{q}^{\alpha_j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \hat{Z}_\beta^{\alpha_j} \quad (70)$$

Summing over constituents yields

$$\nabla \cdot (\varepsilon^\alpha \mathcal{J}^\alpha + \varepsilon^\alpha q_e^\alpha \mathbf{v}^\alpha) + \frac{\partial}{\partial t} (\varepsilon^\alpha q_e^\alpha) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha (\hat{Z}_\beta^\alpha + z^\alpha \hat{e}_\beta^\alpha), \quad (71)$$

where the following restrictions apply

$$\sum_{j=1}^N [\hat{q}^{\alpha_j} + \rho^{\alpha_j} z^{\alpha_j} \hat{r}^{\alpha_j}] = 0 \quad \forall \alpha \quad (72)$$

$$\varepsilon^\alpha \rho^{\alpha_j} (\hat{Z}_\beta^{\alpha_j} + z^{\alpha_j} \hat{e}_\beta^{\alpha_j}) + \varepsilon^\beta \rho^{\beta_j} (\hat{Z}_\alpha^{\beta_j} + z^{\beta_j} \hat{e}_\alpha^{\beta_j}) = 0 \quad j = 1, \dots, N. \quad (73)$$

Equation (73) corresponds precisely with the classical jump condition across a discontinuous interface [15]:

$$\mathbf{n} \cdot [[\mathcal{J} + q_e(\mathbf{v} - \mathbf{w})]] = 0. \quad (74)$$

Linear Momentum Balance

The macroscale linear momentum equation is given by

$$\begin{aligned} & \varepsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j} \mathbf{v}^{\alpha_j}}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha_j}) - \varepsilon^\alpha \rho^{\alpha_j} (\mathbf{g}^{\alpha_j} + \mathbf{g}_I^{\alpha_j}) - \varepsilon^\alpha q_e^{\alpha_j} \mathbf{E}_T \\ & + \frac{1}{2} \varepsilon_0 \mathbf{E}_T \cdot \mathbf{E}^{\alpha_j} \nabla \varepsilon^\alpha - \varepsilon^\alpha \mathbf{P}^{\alpha_j} \cdot \nabla \mathbf{E}_T = \varepsilon^\alpha \rho^{\alpha_j} \hat{\mathbf{i}}^{\alpha_j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \hat{\mathbf{T}}_\beta^{\alpha_j} \end{aligned} \quad (75)$$

where \mathbf{E}_T is the upscaled (total) electric field and is related to the species electric field by $\mathbf{E}_T = \sum_{j=1}^N \sum_{\alpha} \varepsilon^\alpha \mathbf{E}^{\alpha_j}$, and

$$\begin{aligned} \hat{\mathbf{T}}_\beta^{\alpha_j} = & \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[(\mathbf{t}^j)^T + \mathbf{E} \mathbf{D}^j - \frac{1}{2} \varepsilon_0 \mathbf{E}^j \cdot \mathbf{E} \mathbf{I} + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \\ & - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da + \frac{1}{\rho^{\alpha_j}} \hat{d}_\beta^{\alpha_j} \mathbf{E}_T \end{aligned} \quad (76)$$

represents the effect constituent j of phase β has on the rate of change of mechanical momentum of the same constituent in phase α . The relation between the other macroscale variables and their microscale counterparts are given in Appendix C.

There are a couple of additional forces in this form compared to the classical form due to the introduction of the species electric field, $\mathbf{E}^{\alpha j}$, and the volume fraction ε^α . The first we consider an additional (internal) body force, \mathbf{g}_I . It is due to the difference between \mathbf{E} and \mathbf{E}^j (see Appendix C), and so if the source of the electric field is dominated by one charged species, then this term is negligible. The other additional term involves the gradient of the volume fraction. If the medium is homogeneous in volume fraction (ε^α is constant), then this term is zero. The form of this equation is motivated by the form of $\hat{\mathbf{T}}_\beta^{\alpha j}$, which we choose to be consistent with the jump condition associated with momentum balance.

Summing over j yields

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^\alpha) - \varepsilon^\alpha \rho^\alpha (\mathbf{g}^\alpha + \mathbf{g}_I^\alpha) - \varepsilon^\alpha q_e^\alpha \mathbf{E}_T - \varepsilon^\alpha \mathbf{P}^\alpha \cdot \nabla \mathbf{E}_T - \frac{1}{2} \varepsilon_0 \mathbf{E}_T \cdot \mathbf{E}^\alpha \nabla \varepsilon^\alpha = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \hat{\mathbf{T}}_\beta^\alpha, \quad (77)$$

with restrictions

$$\sum_{j=1}^N \rho^{\alpha j} (\hat{\mathbf{i}}^{\alpha j} + \hat{\mathbf{r}}^{\alpha j} \mathbf{v}^{\alpha j}) = 0 \quad \forall \alpha \quad (78)$$

$$\varepsilon^\alpha \rho^{\alpha j} (\hat{\mathbf{T}}_\beta^{\alpha j} + \hat{\mathbf{e}}_\beta^{\alpha j} \mathbf{v}^{\alpha j}) + \varepsilon^\beta \rho^{\beta j} (\hat{\mathbf{T}}_\alpha^{\beta j} + \hat{\mathbf{e}}_\alpha^{\beta j} \mathbf{v}^{\beta j}) = 0 \quad j = 1, \dots, N. \quad (79)$$

The jump condition across a discontinuous interface is [15]:

$$\mathbf{n} \cdot [[\rho \mathbf{v}(\mathbf{v} - \mathbf{w}) - \mathbf{t} - \mathbf{t}_E]] = 0 \quad (80)$$

where \mathbf{w} is the speed of the discontinuity and for the electroquasistatic case considered here,

$$\mathbf{F}_e = \nabla \cdot \mathbf{t}_E = \nabla \cdot (D\mathbf{E} - \frac{1}{2} \varepsilon_0 \mathbf{E} \cdot \mathbf{E} \mathbf{I}). \quad (81)$$

Equation (80) can be shown to correspond directly with (79) using (53).

Angular Momentum Balance

The macroscale form of the conservation of angular momentum equation in indicial notation is

$$-\varepsilon^\alpha \epsilon_{klm} t_{kl}^{\alpha j} - \varepsilon^\alpha \epsilon_{klm} P_k^{\alpha j} (E_T)_l = \varepsilon^\alpha \rho^{\alpha j} \hat{m}_m^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} M_m^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} (\hat{m}_\beta^{\alpha j})_m \quad (82)$$

where the definitions of all variables are given in Appendix C. Thus the macroscale equation is composed of two parts. The equation consisting of all but the term involving $M^{\alpha j}$ is the macroscale form of the microscale equation. The term $M^{\alpha j}$ contains all terms arising from the the microscale conservation of linear

momentum crossed with $\boldsymbol{\xi}$ and volume averaged. These additional terms for the purely mechanical case have been derived before ([16, 22]). The term in \mathbf{M}^{α_j} involving the time rate of change of velocity is known as inertial [16] or local [22] spin. The term in \mathbf{M}^{α_j} involving \mathbf{t}^j has been referred to as the first surface stress moment [16], or apparent couple stress tensor [22]. One observation which is painfully clear is that even in a medium which contains no electric field or charge, the mixture of two media which have symmetric stress tensors may result in a macroscopic medium which has a non-symmetric stress tensor.

Summing over j yields

$$-\varepsilon^\alpha \epsilon_{klm} t_{kl}^\alpha - \varepsilon^\alpha \epsilon_{klm} P_k^\alpha (E_T)_l = \varepsilon^\alpha \rho^{\alpha_j} M_m^\alpha + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha (\widehat{m}_\beta^\alpha)_m \quad (83)$$

where we note that symmetry of the stress tensor is lost due to possible polarization of the medium, the microscale angular momentum, and the interaction of the phase with other phases.

The restriction which must hold to preserve angular momentum within a phase is

$$\sum_{j=1}^N \rho^{\alpha_j} \widehat{\mathbf{m}}^{\alpha_j} = \mathbf{0} \quad \forall \alpha. \quad (84)$$

The restriction which arises from the assumption of no interfacial angular momentum is

$$\varepsilon^\alpha \rho^{\alpha_j} \widehat{\mathbf{m}}_\beta^{\alpha_j} + \varepsilon^\beta \rho^{\alpha\beta} \widehat{\mathbf{m}}_\alpha^{\beta_j} = 0 \quad j = 1, \dots, N. \quad (85)$$

Conservation of Energy

The conservation of energy equation is given by

$$\begin{aligned} \varepsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j} e^{\alpha_j}}{Dt} - \varepsilon^\alpha \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j} - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^{\alpha_j}) - \varepsilon^\alpha \rho^{\alpha_j} h^{\alpha_j} - \varepsilon^\alpha \mathcal{J}^{\alpha_j} \cdot \mathbf{E}_T \\ - \frac{\partial(\varepsilon^\alpha \mathbf{P}^{\alpha_j})}{\partial t} \cdot \mathbf{E}_T - \nabla \cdot (\varepsilon^\alpha \mathbf{v}^{\alpha_j} \mathbf{P}^{\alpha_j}) \cdot \mathbf{E}_T - \frac{1}{2} \varepsilon_0 \mathbf{E}_T \cdot \mathbf{E}^{\alpha_j} \frac{D^{\alpha_j} \varepsilon^\alpha}{Dt} \\ = \varepsilon^\alpha \rho^{\alpha_j} \widehat{Q}^{\alpha_j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \widehat{Q}_\beta^{\alpha_j} \end{aligned} \quad (86)$$

where

$$\begin{aligned} \widehat{Q}_\beta^{\alpha_j} = & \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [\mathbf{q}^j + (\mathbf{t}^j + \mathbf{D}^j \mathbf{E} - \frac{1}{2} \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I}) \cdot \mathbf{v}^j \\ & + \rho^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j + \frac{1}{2} \varepsilon_0 \mathbf{E}^j \cdot \mathbf{E}) (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \\ & - \frac{e^{\alpha_j} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \\ & - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \cdot \int_{\delta A_{\alpha\beta}} \left[(\mathbf{t}^j)^T + \mathbf{E} \mathbf{D}^j - \frac{1}{2} \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I} + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [(-\varepsilon_0 \mathbf{E}^j \mathbf{E} + \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I}) \cdot \mathbf{v}^j + \mathbf{H}^j \times \mathbf{E}] \cdot \mathbf{n}^\alpha da \\
& - \widehat{d}_\beta^{\alpha_j} \mathbf{E}_T \cdot \mathbf{v}^{\alpha_j} - \widehat{\mathbf{h}}_\beta^{\alpha_j} \cdot \mathbf{E}_T
\end{aligned} \tag{87}$$

represents the effect constituent j of phase β has on the rate of change of energy of the same constituent in phase α due to non-mass transfer, non-mechanical means. The relation between the other macroscale variables and their microscale counterparts are given in Appendix C. As in the linear momentum equation, upscaling produces an additional term involving the material time rate of change of the volume fraction. This term would be negligible in a non-swelling porous medium. Additional effects of fluctuations in the species electric work terms manifest themselves in the flux term, \mathbf{q}^{α_j} , and the external source term, h^{α_j} .

Summing over constituents yields

$$\begin{aligned}
\varepsilon^\alpha \rho^\alpha \frac{D^\alpha e^\alpha}{Dt} - \varepsilon^\alpha \mathbf{t}^\alpha : \nabla \mathbf{v}^\alpha - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^\alpha) - \varepsilon^\alpha \rho^\alpha h^\alpha - \varepsilon^\alpha \mathcal{J}^\alpha \cdot \mathbf{E}_T - \frac{\partial(\varepsilon^\alpha \mathbf{P}^\alpha)}{\partial t} \cdot \mathbf{E}_T \\
- \nabla \cdot (\varepsilon^\alpha \mathbf{v}^\alpha \mathbf{P}^\alpha) \cdot \mathbf{E}_T - \frac{1}{2} \varepsilon_0 \mathbf{E}^\alpha \cdot \mathbf{E}_T \frac{D^\alpha \varepsilon^\alpha}{Dt} = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \widehat{Q}_\beta^\alpha \tag{88}
\end{aligned}$$

with the restrictions

$$\sum_{j=1}^N \left[\rho^{\alpha_j} \widehat{Q}^{\alpha_j} + \rho^{\alpha_j} \widehat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \rho^{\alpha_j} \widehat{r}^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j})^2 \right) \right] = 0. \quad \forall \alpha \tag{89}$$

$$\begin{aligned}
& \left[\varepsilon^\alpha \rho^{\alpha_j} \widehat{Q}_\beta^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} \widehat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} \widehat{e}_\beta^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j})^2 \right) \right] \\
& + \left[\varepsilon^\beta \rho^{\beta_j} \widehat{Q}_\alpha^{\beta_j} + \varepsilon^\beta \rho^{\beta_j} \widehat{\mathbf{T}}_\alpha^{\beta_j} \cdot \mathbf{v}^{\beta_j} + \varepsilon^\beta \rho^{\beta_j} \widehat{e}_\alpha^{\beta_j} \left(e^{\beta_j} + \frac{1}{2} (\mathbf{v}^{\beta_j})^2 \right) \right] = 0 \quad j = 1, \dots, N.
\end{aligned} \tag{90}$$

The first restriction states that energy must be conserved within a phase, and the second states that the interface can hold no energy.

We wish to compare (90) with the jump discontinuity condition. Various forms exist depending on what is considered negligible and the use of Maxwell's equations. Here we consider

$$[[\mathbf{q} + \mathbf{t} \cdot \mathbf{v} + (\rho e + \frac{1}{2} \rho v^2)(\mathbf{w} - \mathbf{v}) + \frac{1}{2} \varepsilon_0 (\mathbf{E} \cdot \mathbf{E}) \mathbf{w} + \mathbf{H} \times \mathbf{E} + \mathbf{P} \mathbf{E} \cdot \mathbf{v}]] \cdot \mathbf{n} = 0. \tag{91}$$

Equation (90) can be re-written as:

$$\begin{aligned}
& \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{q}^j + (\mathbf{t}^j + \mathbf{P}^j \mathbf{E}) \cdot \mathbf{v}^j + \rho^j (e^j + \frac{1}{2} (\mathbf{v}^j)^2) (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right. \\
& \quad \left. + \frac{1}{2} \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{w}_{\alpha\beta}^j + \mathbf{H}^j \times \mathbf{E} \right] \cdot \mathbf{n}^\alpha da \\
& = \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{q}^j + (\mathbf{t}^j + \mathbf{P}^j \mathbf{E}) \cdot \mathbf{v}^j + \rho^j (e^j + \frac{1}{2} (\mathbf{v}^j)^2) (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right]
\end{aligned}$$

$$+\frac{1}{2}\varepsilon_0(\mathbf{E}^j \cdot \mathbf{E})\mathbf{w}_{\alpha\beta}^j + \mathbf{H}^j \times \mathbf{E} \Big] \cdot \mathbf{n}^\beta da. \quad (92)$$

Comparing terms we see that the condition involving exchange of energy across the interface, (90), conforms exactly with the classical jump condition (91).

Entropy Balance

The entropy balance for constituent j in phase α is given by

$$\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j} \eta^{\alpha j}}{Dt} - \nabla \cdot \varepsilon^\alpha \phi^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} b^{\alpha j} = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \widehat{\Phi}_\beta^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \widehat{\eta}^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \widehat{\Lambda}^{\alpha j} \quad (93)$$

where $\widehat{\Phi}_\beta^{\alpha j}$ represents the rate at which entropy is gained from constituent j in phase β . Summing over constituents we get

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \eta^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \phi^\alpha) - \varepsilon^\alpha \rho^\alpha b^\alpha = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \widehat{\Phi}_\beta^\alpha + \varepsilon^\alpha \rho^\alpha \widehat{\Lambda}^\alpha, \quad (94)$$

with restrictions

$$\sum_{j=1}^N \rho^{\alpha j} (\widehat{\eta}^{\alpha j} + \widehat{r}^{\alpha j} \eta^{\alpha j}) = 0 \quad \forall \alpha. \quad (95)$$

$$\varepsilon^\alpha \rho^{\alpha j} (\widehat{\Phi}_\beta^{\alpha j} + \widehat{e}_\beta^{\alpha j} \eta^{\alpha j}) + \varepsilon^\beta \rho^{\beta j} (\widehat{\Phi}_\alpha^{\beta j} + \widehat{e}_\alpha^{\beta j} \eta^{\beta j}) = 0 \quad j = 1, \dots, N. \quad (96)$$

The second condition is exactly analogous to the classical jump boundary condition applied at an interface. This equation can be used to obtain restrictions on the forms of constitutive equations using, for example, the Coleman and Noll method (see e.g. [4, 13]). At this point we make no assumptions regarding the form of the entropy flux or source. It is now postulated that the rate of entropy production is non-negative after summing over both species and phases. Our statement at the end of Section 2 need not hold in this case, as it is the rate of entropy production of the universe which is non-negative.

4 Discussion

We have provided the microscale and macroscale balance laws for a multiphase, multi-species, swelling system which incorporates electroquasistatics. The microscale derivation follows the approach of Eringen and Maugin [15], while the upscaling to the macroscale is achieved via spatial averaging. The species electric field, $\mathbf{E}^{\alpha j}$, is carefully defined and the complete relations between the microscopic and macroscopic variables and the species and bulk phase variables are provided. Further comparisons were made between restrictions required to hold at interfaces and jump conditions classically used at interfaces.

In regards to the conservation of momentum and energy, there are several ways in which one can group together terms into the definitions of the macroscopic variables. In this paper, we choose the macroscopic definitions in a way which results in consistency between restriction conditions at interfaces and classical jump conditions used at interfaces. But as a consequence, additional body sources appear due not to external sources but due to species electric fields and microscopic fluctuations of the work terms. Further, there are additional terms which appear due to gradients in volume fractions and material time rate-of-change of the volume fractions in the conservation of momentum and energy equation, respectively. This is *not* due to the primitive choice of \mathbf{F}_e^j and W_e^j (see equations (33-35)). Rather it is a consequence of the choice of grouping terms so as to recover classical jump conditions. The consequence of these additional terms needs to be investigated. This is partially done in part II of these papers.

The field equations are required for many practical applications including, but not limited to, swelling clays (smectites), biopolymers, biological membranes, pulsed electrophoresis, and chromatography. In part II of these papers we exploit the entropy inequality with independent variables consistent with several natural systems and apply the resulting constitutive theory near equilibrium for two problems: electrolyte transport in swelling clays and pulsed electrophoresis.

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Appendix A. Nomenclature

Superscripts, Subscripts, and Other Notations

- \cdot^{α_j} j^{th} component of α -phase on mesoscale
- \cdot^{α} α -phase on mesoscale
- \sim fluctuation from averaged quantity
- $\hat{\cdot}$ denotes exchange from other interface or phase
- $\cdot^{k,l}$ difference of the two quantities, i.e. $\cdot^k - \cdot^l$
- $\cdot|_{\alpha_j}$ microscopic property of constituent j in phase [subscript] (non-averaged)

Latin Symbols

- $\delta A_{\alpha\beta}$: Portion of $\alpha\beta$ -interface in representative elementary volume (REV)
- b^{α_j}, b^{α} : External entropy source [J/(Kg-s-°K)]
- C^{α_j} : Mass fraction of j^{th} component [-]
- D^{α_j}, D^{α} : Electric displacement [C/m²]
- \hat{d}^{α_j} : Net effect other constituents have on the charge of constituent j within phase α in Gauss' Law [C]
- $\hat{d}_{\beta}^{\alpha_j}$: Net effect phase β has on the charge of constituent j in phase α in Gauss' Law [C]

e^{α_j}, e^α : energy density [J/Kg]

$\widehat{e}_\beta^{\alpha_j}$: Rate of mass transfer from phase [subscript] to phase [superscript] per unit mass density [1/s]

$\mathbf{E}^{\alpha_j}, \mathbf{E}^\alpha$: Electric Field intensity generated by (the j th constituent of) phase α [V/m]

$\mathbf{g}^{\alpha_j}, \mathbf{g}^\alpha$: External supply of momentum (gravity) [m/s²]

$\mathbf{g}_I^{\alpha_j}, \mathbf{g}_I^\alpha$: Internal supply of momentum due to fluctuations in Kelvin and Lorentz forces [m/s²]

h^{α_j}, h^α : External supply of energy [J/(Kg-s)]

$\widehat{\mathbf{h}}^{\alpha_j}, \widehat{\mathbf{h}}^\alpha$: Free current density induces by other species within the same phase within Ampère's law [A/m²]

$\widehat{\mathbf{h}}_\beta^{\alpha_j}, \widehat{\mathbf{h}}_\beta^\alpha$: Free current density induces by other phases on species j in Ampère's law [A/m²]

$\widehat{\mathbf{i}}^{\alpha_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

$\mathbf{H}^{\alpha_j}, \mathbf{H}^\alpha$: Magnetic field intensity [A/m]

$\widehat{\mathbf{i}}^{\alpha_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

$\mathbf{J}^{\alpha_j}, \mathbf{J}^\alpha$: Free current density in a fixed frame of reference [A/m²]

$\mathcal{J}^{\alpha_j}, \mathcal{J}^\alpha$: Free current density in the material frame of reference [A/m²] = [C/m²-s]; $\mathcal{J}^{\alpha_j} = \mathbf{J}^{\alpha_j} - q_e^{\alpha_j} \mathbf{v}^{\alpha_j}$

$\widehat{\mathbf{m}}^{\alpha_j}$: Rate of angular momentum gain due to interaction with other species within the same phase per unit mass density [N-m/Kg]

$\widehat{\mathbf{m}}_\beta^{\alpha_j}$: Rate of angular momentum gain by constituent j in phase α due to interaction with phase β [N-m/Kg]

\mathbf{M}^{α_j} : Rate of angular momentum gain due to the microscale angular momentum terms - see Appendix C [N-m/Kg]

\mathbf{n}^α : Unit normal vector pointing out of α -phase within mesoscopic REV [-]

$\mathbf{P}^{\alpha_j}, \mathbf{P}^\alpha$: Polarization density averaged over α -phase [C/m²]

$q_e^{\alpha_j}, q_e^\alpha$: Charge density averaged over α -phase [C/m³]

- $\widehat{\mathbf{m}}^{\alpha j}$: Rate of gain of angular momentum of constituent j from other constituents in phase α [m^2/s^2]
- $\mathbf{q}^{\alpha j}$: Partial heat flux vector for the j^{th} component of phase α [$\text{J}/(\text{m}^2\text{-s})$]
- \mathbf{q}^α : Heat flux vector for phase α [$\text{J}/(\text{m}^2\text{-s})$]
- $\widehat{q}^{\alpha j}$: Net rate of charge density gain by species j due to interaction with other species within phase α (does not include that gained to due mass transfer). [$\text{C}/\text{m}^3\text{-s}$]
- $\widehat{Q}^{\alpha j}$: Rate of energy gain due to interaction with other species within the same phase per unit mass density not due to mass or momentum transfer [$\text{J}/(\text{Kg-s})$]
- $\widehat{Q}_\beta^{\alpha j}, \widehat{Q}_\beta^\alpha$: Energy transfer rate from phase [subscript] to phase [superscript] per unit mass density not due to mass or momentum transfer [$\text{J}/(\text{Kg-s})$]
- \mathbf{r} : Microscale spatial variable [m]
- $\widehat{r}^{\alpha j}$: Rate of mass gain due to interaction with other species within the same phase per unit mass density [$1/\text{s}$]
- t : Time [s]
- T : Temperature [$^\circ\text{K}$]
- $\mathbf{t}^{\alpha j}$: Partial stress tensor for the j^{th} component for phase α [N/m^2]
- \mathbf{t}^α : Total stress tensor for the phase [N/m^2]
- $\widehat{\mathbf{T}}_\beta^{\alpha j}, \widehat{\mathbf{T}}_\beta^\alpha$: Rate of momentum transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass density [N/Kg]
- $\mathbf{v}^{\alpha j}, \mathbf{v}^\alpha$: Velocity [m/s]
- δV : Representative elementary volume (REV)
- δV_α : Portion of α -phase in REV
- $\mathbf{w}_{\alpha\beta}^j$: Velocity of constituent j at interface between phases α and β [m/s]
- \mathbf{x} : Macroscale spatial variable [m]
- $z^{\alpha j}$: Charge per unit mass density of constituent j in phase α [C/Kg], $q_e^{\alpha j} = \rho^{\alpha j} z^{\alpha j}$
- $\widehat{Z}_\beta^{\alpha j}, \widehat{Z}_\beta^\alpha$: Rate of exchange of charge of constituent j from phase β to phase α per unit mass [$\text{C}/\text{Kg-s}$]

Greek Symbols

- γ^α : Indicator function which is 1 if in mesoscopic region α and zero otherwise
- ε^α : Volume fraction of α -phase in mesoscale REV [-]
- ε_0 : Permittivity in a vacuum. In MKS units, the permittivity has the value of 8.854×10^{-12} Farads per meter.
- ϵ_{klm} : Permutation tensor
- $\hat{\Lambda}^{\alpha_j}, \hat{\Lambda}^\alpha$: Entropy production per unit mass density [J/(Kg-s-°K)]
- ξ : Microscale spatial variable which varies over REV for fixed \mathbf{x} : $\mathbf{r} = \mathbf{x} + \xi$ [m]
- $\eta^{\alpha_j}, \eta^\alpha$: Entropy [J/(Kg-°K)]
- $\hat{\eta}^{\alpha_j}$: Entropy gain due to interaction with other species within the same phase/interface per unit mass density [J/(Kg-s-°K)]
- ϕ^{α_j} : Partial entropy flux vector for the j^{th} component for phase [J/(m²-s-°K)]
- ϕ^α : Total entropy flux vector for the phase [J/(m²-s-°K)]
- $\hat{\Phi}_\beta^{\alpha_j}, \hat{\Phi}_\beta^\alpha$: Entropy transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass [J/(kg-s-°K)]
- ρ^{α_j} : Partial mass density of j^{th} component of α -phase [Kg/m³] so that $\varepsilon^\alpha \rho^{\alpha_j}$ is the total mass of j^{th} constituent in phase α divided by the volume of REV
- ρ^α : Mass density of α -phase averaged over α -phase [Kg/m³]
- $\hat{\sigma}^{\alpha_j}$: Induced curl of electric field of species j due to presence of other species within the same phase. See Faraday's law. [V/m]
- $\hat{\sigma}_\beta^{\alpha_j}$: Effect constituent j of phase β has on the curl of the electric field of phase α [V/m]

Appendix B. Definition of Macroscopic Bulk Variables

The relationships between the macroscopic constituent variables and their bulk counterparts follow:

$$\rho^\alpha = \sum_{j=1}^N \rho^{\alpha_j}, \quad (\text{B.1})$$

$$C^{\alpha_j} = \frac{\rho^{\alpha_j}}{\rho^\alpha}, \quad (\text{B.2})$$

$$\mathbf{v}^\alpha = \sum_{j=1}^N C^{\alpha_j} \mathbf{v}^{\alpha_j}, \quad (\text{B.3})$$

$$\hat{\mathbf{e}}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \hat{\mathbf{e}}_\beta^{\alpha_j}, \quad (\text{B.4})$$

$$\mathbf{J}^\alpha = \sum_{j=1}^N \mathbf{J}^{\alpha_j} \quad (\text{B.5})$$

$$\mathcal{J}^\alpha = \sum_{j=1}^N \mathcal{J}^{\alpha_j} + q_e^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}, \quad (\text{B.6})$$

$$\mathbf{D}^\alpha = \sum_{j=1}^N \mathbf{D}^{\alpha_j} \quad (\text{B.7})$$

$$\mathbf{P}^\alpha = \sum_{j=1}^N \mathbf{P}^{\alpha_j} \quad (\text{B.8})$$

$$\mathbf{E}^\alpha = \sum_{j=1}^N \mathbf{E}^{\alpha_j} \quad (\text{B.9})$$

$$q_e^\alpha = \sum_{j=1}^N q_e^{\alpha_j}, \quad (\text{B.10})$$

$$\hat{d}_\beta^\alpha = \sum_{j=1}^N \hat{d}_\beta^{\alpha_j} \quad (\text{B.11})$$

$$\hat{\sigma}_\beta^\alpha = \sum_{j=1}^N \hat{\sigma}_\beta^{\alpha_j} \quad (\text{B.12})$$

$$\mathbf{H}^\alpha = \sum_{j=1}^N (\mathbf{H}^{\alpha_j} - \mathbf{P}^{\alpha_j} \times \mathbf{v}^{\alpha_j, \alpha}) \quad (\text{B.13})$$

$$\hat{\mathbf{h}}_\beta^\alpha = \sum_{j=1}^N \hat{\mathbf{h}}_\beta^{\alpha_j} \quad (\text{B.14})$$

$$z^\alpha = \sum_{j=1}^N C^{\alpha_j} z^{\alpha_j} \quad (\text{B.15})$$

$$\hat{Z}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} (\hat{Z}_\beta^{\alpha_j} + \hat{\mathbf{e}}_\beta^{\alpha_j} z^{\alpha_j, \alpha}) \quad (\text{B.16})$$

$$\mathbf{t}^\alpha = \sum_{j=1}^N [\mathbf{t}^{\alpha_j} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \mathbf{v}^{\alpha_j, \alpha}], \quad (\text{B.17})$$

$$\mathbf{g}^\alpha = \sum_{j=1}^N C^{\alpha_j} \mathbf{g}^{\alpha_j}, \quad (\text{B.18})$$

$$\mathbf{g}_I^\alpha = \sum_{j=1}^N C^{\alpha_j} \mathbf{g}_I^{\alpha_j} \quad (\text{B.19})$$

$$\hat{\mathbf{T}}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \left(\hat{\mathbf{T}}_\beta^{\alpha_j} + \hat{\mathbf{e}}_\beta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \right) + \frac{1}{\rho^\alpha} \hat{d}_\beta^\alpha \mathbf{E}_T, \quad (\text{B.20})$$

$$\hat{\mathbf{m}}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \hat{\mathbf{m}}_\beta^{\alpha_j}, \quad (\text{B.21})$$

$$\mathbf{M}^\alpha = \sum_{j=1}^N C^{\alpha_j} \mathbf{M}^{\alpha_j}, \quad (\text{B.22})$$

$$e^\alpha = \sum_{j=1}^N C^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right), \quad (\text{B.23})$$

$$\mathbf{q}^\alpha = \sum_{j=1}^N \left[\mathbf{q}^{\alpha_j} + \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) + \mathbf{v}^{\alpha_j, \alpha} \mathbf{P}^{\alpha_j} \cdot \mathbf{E}_T \right], \quad (\text{B.24})$$

$$h^\alpha = \sum_{j=1}^N C^{\alpha_j} (h^{\alpha_j} + (\mathbf{g}^{\alpha_j} + \mathbf{g}_I^{\alpha_j}) \cdot \mathbf{v}^{\alpha_j, \alpha}), \quad (\text{B.25})$$

$$\begin{aligned} \hat{Q}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \left[\hat{Q}_\beta^{\alpha_j} + \hat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \hat{\mathbf{e}}_\beta^{\alpha_j} \left(e^{\alpha_j, \alpha} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right. \\ \left. - \hat{d}_\beta^\alpha \mathbf{E}_t \cdot \mathbf{v}^\alpha - \hat{\mathbf{h}}_\beta^\alpha \cdot \mathbf{E}_T \right], \end{aligned} \quad (\text{B.26})$$

$$\eta^\alpha = \sum_{j=1}^N C^{\alpha_j} \eta^{\alpha_j}, \quad (\text{B.27})$$

$$\phi^\alpha = \sum_{j=1}^N (\phi^{\alpha_j} - \rho^{\alpha_j} \eta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}), \quad (\text{B.28})$$

$$b^\alpha = \sum_{j=1}^N C^{\alpha_j} b^{\alpha_j}, \quad (\text{B.29})$$

$$\hat{\Phi}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \left(\hat{\Phi}_\beta^{\alpha_j} + \hat{\mathbf{e}}_\beta^{\alpha_j} \eta^{\alpha_j, \alpha} \right), \quad (\text{B.30})$$

$$\widehat{\Lambda}^\alpha = \sum_{j=1}^N C^{\alpha j} \widehat{\Lambda}^{\alpha j}, \quad (\text{B.31})$$

$$(\text{B.32})$$

Appendix C. Relationship between Macroscopic and Microscopic Variables

For notational brevity, define the volume average over phase α with angle brackets:

$$\langle \psi^j \rangle^\alpha(\mathbf{x}, t) = \frac{1}{|\delta V_\alpha|} \int_{\delta V} \psi^j(\mathbf{r}, t) \gamma_\alpha(\mathbf{r}, t) dv(\boldsymbol{\xi}) \quad (\text{C.1})$$

so that if for example, ρ^j is constant throughout phase α then $\langle \rho^j \rangle^\alpha$ would be that constant density.

Similarly we define the mass average to be

$$\overline{\psi^j}^\alpha(\mathbf{x}, t) = \frac{1}{\langle \rho^j \rangle^\alpha |\delta V_\alpha|} \int_{\delta V} \rho^j(\mathbf{r}, t) \psi^j(\mathbf{r}, t) \gamma_\alpha(\mathbf{r}, t) dv(\boldsymbol{\xi}). \quad (\text{C.2})$$

Thus for example, while the volume average of velocity makes no physical sense, the mass average (momentum) does.

The relationships between the macroscopic constituent variables and their microscopic counterparts follow. There are *no* assumptions made about small fluctuations about the average. What follows is exact.

$$\rho^{\alpha j} = \langle \rho^j \rangle^\alpha \quad (\text{C.3})$$

$$\mathbf{v}^{\alpha j} = \overline{\mathbf{v}^j}^\alpha \quad (\text{C.4})$$

$$\widehat{\mathbf{r}}^{\alpha j} = \overline{\widehat{\mathbf{r}}^j}^\alpha \quad (\text{C.5})$$

$$\widehat{\mathbf{e}}_\beta^{\alpha j} = \frac{1}{\rho^{\alpha j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \quad (\text{C.6})$$

$$\mathbf{J}^{\alpha j} = \langle \mathbf{J}^j \rangle^\alpha \quad (\text{C.7})$$

$$\mathcal{J}^{\alpha j} = \langle \mathcal{J}^j \rangle^\alpha + \langle q_e^j \mathbf{v}^j \rangle^\alpha - q_e^{\alpha j} \mathbf{v}^{\alpha j} \quad (\text{C.8})$$

$$\mathcal{D}^{\alpha j} = \langle \mathcal{D}^j \rangle^\alpha \quad (\text{C.9})$$

$$\mathbf{D}^{\alpha j} = \langle \mathbf{D}^j \rangle^\alpha \quad (\text{C.10})$$

$$\mathbf{P}^{\alpha j} = \langle \mathbf{P}^j \rangle^\alpha \quad (\text{C.11})$$

$$\mathbf{E}^{\alpha j} = \langle \mathbf{E}^j \rangle^\alpha \quad (\text{C.12})$$

$$\mathbf{E}_T = \sum_\alpha \varepsilon^\alpha \langle \mathbf{E} \rangle^\alpha = \frac{1}{|\delta V|} \int_{\delta V} \mathbf{E} dv \quad (\text{C.13})$$

$$q_e^{\alpha j} = \langle q_e^j \rangle^\alpha \quad (\text{C.14})$$

$$\widehat{d}^{\alpha_j} = \langle \widehat{d}^j \rangle^\alpha \quad (\text{C.15})$$

$$\widehat{d}_\beta^{\alpha_j} = -\frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \mathbf{D}^j \cdot \mathbf{n}^\alpha da \quad (\text{C.16})$$

$$\widehat{\sigma}^{\alpha_j} = \langle \widehat{\sigma}^j \rangle^\alpha \quad (\text{C.17})$$

$$\widehat{\sigma}_\beta^{\alpha_j} = -\frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \mathbf{n}^\alpha \times \mathbf{E}^j da \quad (\text{C.18})$$

$$\mathbf{H}^{\alpha_j} = \langle \mathbf{H}^j \rangle^\alpha + [\mathbf{P}^{\alpha_j} \times \mathbf{v}^{\alpha_j} - \langle \mathbf{P}^j \times \mathbf{v}^j \rangle^\alpha] \quad (\text{C.19})$$

$$\widehat{\mathbf{h}}_\beta^{\alpha_j} = \frac{1}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [\mathbf{D}^j \mathbf{w}_{\alpha\beta}^j \cdot \mathbf{n}^\alpha - (\mathbf{H}^j - \mathbf{P}^j \times \mathbf{v}^j) \times \mathbf{n}^\alpha] da \quad (\text{C.20})$$

$$\widehat{\mathbf{h}}^{\alpha_j} = \langle \widehat{\mathbf{h}}^j \rangle^\alpha \quad (\text{C.21})$$

$$z^{\alpha_j} = \overline{z^j} \quad (\text{C.22})$$

$$\widehat{q}^{\alpha_j} = \langle \widehat{q}_e^j \rangle^\alpha + \varepsilon^\alpha \rho^{\alpha_j} \overline{z^j \widehat{r}^j}^\alpha - \varepsilon^\alpha \rho^{\alpha_j} \widehat{r}^{\alpha_j} z^{\alpha_j} \quad (\text{C.23})$$

$$\begin{aligned} \widehat{Z}_\beta^{\alpha_j} &= \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [q_e^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) - \mathcal{J}^j] \cdot \mathbf{n}^\alpha da \\ &\quad - \frac{z^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [\rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \end{aligned} \quad (\text{C.24})$$

$$\begin{aligned} \mathbf{t}^{\alpha_j} &= \langle \mathbf{t}^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j} - \rho^{\alpha_j} \overline{\mathbf{v}^j \mathbf{v}^j}^\alpha + \langle \mathbf{D}^j \mathbf{E} \rangle^\alpha - \mathbf{D}^{\alpha_j} \mathbf{E}_T \\ &\quad + \frac{1}{2} \varepsilon_0 [\mathbf{E}^{\alpha_j} \cdot \mathbf{E}_T - \langle \mathbf{E}^j \cdot \mathbf{E} \rangle^\alpha] \mathbf{I} \end{aligned} \quad (\text{C.25})$$

$$\mathbf{g}^{\alpha_j} = \overline{\mathbf{g}^j}^\alpha \quad (\text{C.26})$$

$$\mathbf{g}_I^{\alpha_j} = \frac{\varepsilon_0}{2\rho^{\alpha_j}} [\nabla \mathbf{E}_T \cdot \mathbf{E}^{\alpha_j} - \langle \nabla \mathbf{E} \cdot \mathbf{E}^j \rangle^\alpha - \nabla \mathbf{E}^{\alpha_j} \cdot \mathbf{E}_T + \langle \nabla \mathbf{E}^j \cdot \mathbf{E} \rangle^\alpha] \quad (\text{C.27})$$

$$\widehat{\mathbf{i}}^{\alpha_j} = \overline{\widehat{\mathbf{i}}^j}^\alpha + \overline{\widehat{\mathbf{r}}^j \mathbf{v}^j}^\alpha - \widehat{\mathbf{r}}^{\alpha_j} \mathbf{v}^{\alpha_j} + \frac{1}{\rho^{\alpha_j}} (\widehat{d}^{\alpha_j} \mathbf{E}_T - \langle \widehat{d}^j \mathbf{E} \rangle^\alpha) \quad (\text{C.28})$$

$$\begin{aligned} \widehat{\mathbf{T}}_\beta^{\alpha_j} &= \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[(\mathbf{t}^j)^T + \mathbf{E} \mathbf{D}^j - \frac{1}{2} \varepsilon_0 \mathbf{E}^j \cdot \mathbf{E} \mathbf{I} + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \\ &\quad - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da + \frac{1}{\rho^{\alpha_j}} \widehat{d}_\beta^{\alpha_j} \mathbf{E}_T \end{aligned} \quad (\text{C.29})$$

$$\widehat{\mathbf{m}}^{\alpha_j} = \langle \widehat{\mathbf{m}}^j \rangle^\alpha - \frac{1}{\rho^j} [\langle \mathbf{P}^j \times \mathbf{E}^j \rangle^\alpha - \mathbf{P}^{\alpha_j} \times \mathbf{E}^{\alpha_j}] \quad (\text{C.30})$$

$$(\widehat{m}_\beta^{\alpha_j})_m = \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [\epsilon_{klm} \xi_k (t_{nl} + v_l ((w_{\alpha\beta}^j)_n - v_n^j))] n_n da \quad (\text{C.31})$$

$$\begin{aligned} (M^{\alpha_j})_m &= -\frac{\partial}{\partial t} \left(\varepsilon^\alpha \rho^{\alpha_j} \overline{\epsilon_{klm} \xi_k v_l^j}^\alpha \right) - \left[\varepsilon^\alpha \rho^{\alpha_j} \overline{v_n^j (\epsilon_{klm} \xi_k v_l^j)}^\alpha \right]_{,n} \\ &\quad + \left[\varepsilon^\alpha \langle \epsilon_{klm} \xi_k \mathbf{t}_{nl}^j \rangle^\alpha \right]_{,n} + \varepsilon^\alpha \rho^{\alpha_j} \overline{\epsilon_{klm} \xi_k g_l^j}^\alpha + \varepsilon^\alpha \langle \epsilon_{klm} \xi_k (F_e^j)_l \rangle^\alpha \\ &\quad + \varepsilon^\alpha \langle \epsilon_{klm} \xi_k (\rho^j \widehat{v}_k^j + \rho^j \widehat{r}^j v_k^j) \rangle^\alpha \end{aligned} \quad (\text{C.32})$$

$$e^{\alpha_j} = \overline{e^j}^\alpha + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \frac{\varepsilon_0}{\rho^{\alpha_j}} [\langle \mathbf{E}^j \cdot \mathbf{E} \rangle^\alpha - \mathbf{E}^{\alpha_j} \cdot \mathbf{E}_T] \quad (\text{C.33})$$

$$\begin{aligned} \mathbf{q}^{\alpha_j} = & \langle \mathbf{q}^j \rangle^\alpha + \langle \mathbf{t}^j \cdot \mathbf{v}^j \rangle^\alpha - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} (e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}) - \rho^{\alpha_j} \mathbf{v}^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \\ & + \langle \mathbf{E} \times \mathbf{H}^j \rangle^\alpha - \mathbf{E}_T \times \mathbf{H}^{\alpha_j} + \langle \mathbf{P}^j \mathbf{v}^j \cdot \mathbf{E} \rangle^\alpha - \mathbf{P}^{\alpha_j} \mathbf{v}^{\alpha_j} \cdot \mathbf{E}_T \end{aligned} \quad (\text{C.34})$$

$$\begin{aligned} h^{\alpha_j} = & \overline{h^j}^\alpha + \overline{\mathbf{g}^j \cdot \mathbf{v}^j}^\alpha - \overline{\mathbf{g}^j}^\alpha \cdot \mathbf{v}^{\alpha_j} \\ & + \frac{\varepsilon_0}{2\rho^{\alpha_j}} \left[\frac{\partial \mathbf{E}^{\alpha_j}}{\partial t} \cdot \mathbf{E}_T - \left\langle \frac{\partial \mathbf{E}^j}{\partial t} \cdot \mathbf{E}_T \right\rangle^\alpha + \left\langle \frac{\partial \mathbf{E}}{\partial t} \cdot \mathbf{E}^j \right\rangle^\alpha - \frac{\partial \mathbf{E}_T}{\partial t} \cdot \mathbf{E}^{\alpha_j} \right] \end{aligned} \quad (\text{C.35})$$

$$\begin{aligned} \widehat{Q}^{\alpha_j} = & \widehat{Q}^j^\alpha + \widehat{\mathbf{i}}^j \cdot \mathbf{v}^j - \widehat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \widehat{r}^j - (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \widehat{r}^{\alpha_j} \\ & + \frac{1}{\rho^{\alpha_j}} [\langle \widehat{\mathbf{h}}^j \cdot \mathbf{E} \rangle^\alpha - \widehat{\mathbf{h}}^{\alpha_j} \cdot \mathbf{E}_T] \end{aligned} \quad (\text{C.36})$$

$$\begin{aligned} \widehat{Q}_\beta^{\alpha_j} = & \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [\mathbf{q}^j + (\mathbf{t}^j + \mathbf{D}^j \mathbf{E} - \frac{1}{2} \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I}) \cdot \mathbf{v}^j \\ & + \rho^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j + \frac{1}{2} \varepsilon_0 \mathbf{E}^j \cdot \mathbf{E}) (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \\ & - \frac{e^{\alpha_j} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \\ & - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \cdot \int_{\delta A_{\alpha\beta}} \left[(\mathbf{t}^j)^T + \mathbf{E} \mathbf{D}^j - \frac{1}{2} \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I} + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \\ & + \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} [(-\varepsilon_0 \mathbf{E}^j \mathbf{E} + \varepsilon_0 (\mathbf{E}^j \cdot \mathbf{E}) \mathbf{I}) \cdot \mathbf{v}^j + \mathbf{H}^j \times \mathbf{E}] \cdot \mathbf{n}^\alpha da \\ & - \widehat{d}_\beta^{\alpha_j} \mathbf{E}_T \cdot \mathbf{v}^{\alpha_j} - \widehat{\mathbf{h}}_\beta^{\alpha_j} \cdot \mathbf{E}_T \end{aligned} \quad (\text{C.37})$$

$$\eta^{\alpha_j} = \overline{\eta^j}^\alpha \quad (\text{C.38})$$

$$\phi^{\alpha_j} = \langle \phi^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \eta^{\alpha_j} - \rho^{\alpha_j} \overline{\mathbf{v}^j \eta^j}^\alpha \quad (\text{C.39})$$

$$b^{\alpha_j} = \overline{b^j}^\alpha \quad (\text{C.40})$$

$$\begin{aligned} \widehat{\Phi}^{\alpha_j} = & \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} [\phi^j + \rho^j \eta^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da - \frac{\eta^{\alpha_j}}{|\delta V|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \end{aligned} \quad (\text{C.41})$$

$$\widehat{\eta}^{\alpha_j} = \varepsilon^\alpha \rho^{\alpha_j} (\widehat{\eta}^j^\alpha + \widehat{r}^j \eta^j - \widehat{r}^{\alpha_j} \eta^{\alpha_j}) \quad (\text{C.42})$$

$$\widehat{\Lambda}^{\alpha_j} = \overline{\Lambda^j}^\alpha \quad (\text{C.43})$$